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| <b>(54) Title:</b> BIAXIALLY-ORIENTED POLYPROPYLENE FILM WITH IMPROVED GAS BARRIER<br><br><b>(57) Abstract</b><br><br>A biaxially-oriented polypropylene (BOPP) film with improved barrier properties, and a process for making the film. The MVTR of a multilayer BOPP film is improved by blending wax in the core layer resin, and providing a polyolefin cap layer on each side of the core layer. Significant additional improvements are seen when the film is heated at an elevated temperature for an extended time.   |           |  |

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# "BIAXIALLY-ORIENTED POLYPROPYLENE FILM WITH IMPROVED GAS BARRIER"

## BACKGROUND OF THE INVENTION

### Field of the Invention

5           This invention relates to a polyolefin film structure with improved barrier properties. In one aspect, the invention concerns a process for making a multi-layer biaxially-oriented polypropylene film by incorporating in a core layer  
10   minor amounts of wax to improve the moisture barrier.

### Description of Related Art

          Biaxially-oriented polypropylene (BOPP) films are widely used in packaging because they have  
15   good stiffness, strength, optical properties (low haze and high gloss), and moisture barrier properties. Good resistance to moisture transmission, as measured by the "moisture vapor transmission rate" (MVTR), is quite desirable in  
20   packaging of food items containing salt or sugar or ingredients that are inherently hygroscopic. Conversely, an item packaged with a specific, intended moisture content will be better able to maintain that required moisture and not dry out if  
25   it is packaged with a high moisture barrier film. An essential purpose of the BOPP barrier film is to extend the package shelf life.

          Since barrier properties vary as the inverse of film thickness, a thicker film made  
30   either by direct film extrusion and orientation or by lamination of two or more films can be expected to have an improved MVTR. Although these thicker

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films remain clear, haze and gloss properties can suffer. Small improvements come at significant expense, as film costs increase proportionately with thickness.

5                   One important method to reduce MVTR in BOPP packaging films is to coat the film with a thin layer of metal, e.g., aluminum, which can result in four to ten-fold improvements in MVTR values. Such metallized film then becomes opaque, however, and  
10 the package contents cannot be viewed.

Resistance to moisture and especially oxygen transmission can also be improved by coating a BOPP film with poly(vinylidene chloride) ("PVDC"), or less commonly by coextruding a layer of PVDC or  
15 its copolymers with polypropylene followed by orientation of the film. While such films are useful, they have several disadvantages. First, an adhesive or tie-layer is often needed to prevent delamination of layers of these two incompatible  
20 materials. Second, relatively thin coatings of PVDC provide an MVTR reduction of only a factor of two or three at best. Finally, the chloride in PVDC discourages recycling of the films.

Packaging films incorporating layers of  
25 poly(vinyl alcohol) ("PVA") or copolymers of ethylene and vinyl alcohol ("EVOH") can provide excellent oxygen barrier, but are unsuitable for high moisture barrier. The PVA or EVOH layers must be sandwiched between polyolefin layers to protect  
30 the PVA or EVOH from absorbing moisture and thereby losing the oxygen barrier. As with PVDC films, these films also require adhesive layers or tie-layers to prevent delamination.

Yet another approach, as taught in U.S.  
35 4,921,749 to Bossaert et al., assigns to Exxon

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Chemical Patents Inc., has been to add to a polypropylene base layer a low molecular weight modifier such as hydrogenated petroleum resin in an amount from 3 to 30% by weight. The film is then  
5 biaxially-oriented and is said to achieve a 40% reduction in MVTR. However, this technique is subject to evolution of smoke and plateout on equipment during production, and is relatively costly at the concentrations of hydrocarbon resin  
10 used.

More recent work in U.S. 5,155,160 to Yeh et al. shows that the barrier properties of polyolefin films can be reduced by a factor of four or more if a partially incompatible wax is added,  
15 generally in an amount between about two and twelve percent, to the polyolefin.

When the materials taught by Bossaert et al. '749 and by Yeh et al. '160 are added to polypropylene film, particularly at the higher  
20 percentages taught therein, film shrinkage becomes an issue. In most packaging applications, good film dimensional stability is desired to avoid distortion of the package. These additives often migrate to the film surface where they may transfer to and  
25 "plate out" on packaging equipment or the goods themselves. Moreover, the surface properties of the film such as the coefficient of friction (slipperiness), film stiffness, heat seal characteristics, and printability can be adversely  
30 affected.

Therefore, it is an object of the invention to produce a biaxially-oriented polypropylene film which has good processing characteristics in combination with an improved  
35 moisture barrier.

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## SUMMARY OF THE INVENTION

It has now been discovered the moisture barrier of biaxially-oriented polypropylene (BOPP) films can be improved by incorporating wax in an amount less than that previously believed to be effective. Wax is blended with the core layer resin and cap layers are added to produce a multi-layer BOPP film.

The new process for making a thermoplastic film comprises forming a blend of a polypropylene resin and from 0.25 to 15 weight percent of a wax, extruding the blend to form a core layer of a film, orienting the core layer in biaxial directions, and providing on each side of the core layer a polyolefin cap layer. The resin is selected from the group consisting of isotactic homopolymers of propylene, copolymers of propylene with up to fifteen percent ethylene or butene, terpolymers of propylene with ethylene and butene, and mixtures thereof. The wax is incompatible with the resin and has an average molecular weight from 300 to 1000.

Significant additional improvements can be achieved when the film is heated at an elevated temperature for an extended time.

## 25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention involves a process for making multi-layer sheet or film having at least three layers, as described below.

Core layer resin

30 The interior layer, or one of the interior layers if more than one, is called the "core" layer and comprises polypropylene. The term

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"polypropylene" as used herein is a generic reference to a semi-crystalline polymer with a majority of polymerized propylene, specifically including the isotactic homopolymers of propylene, 5 copolymers of propylene with up to fifteen percent ethylene or butene, terpolymers of propylene with ethylene and butene, and mixtures thereof.

Preferred resins are those selected from propylene homopolymers and from copolymers of 10 propylene with up to six percent comonomer such as ethylene or butene. Melt Flow Rates of 1-15, preferably from 1.5 to 6, are suitable for sheet or blown film. Examples of suitable commercial polypropylenes include Quantum 7300, Amoco 6314, 15 Solvay 2108, and Fina 3275.

#### Wax

The polypropylene core layer contains a small amount of an incompatible wax. By "incompatible" is meant that the wax has only 20 limited solubility with the polypropylene. Both natural and synthetic waxes can be employed, including petroleum waxes such as paraffin wax (predominantly straight-chain saturated hydrocarbons) and microcrystalline wax 25 (predominantly cyclic saturated hydrocarbons with isoparaffins), vegetable waxes (e.g., carnauba), mineral waxes, and animal waxes (e.g., spermaceti) waxes. Paraffins and polyethylene waxes are preferred.

30 Waxes with a crystalline morphology appear to provide better moisture barrier in this invention. While not intending to be bound by theory, a preferred wax such as linear, highly-crystalline polyethylene is believed to remain 35 incompatible with the crystalline regions of

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polypropylene, and will concentrate in the amorphous regions of the resin. Furthermore, the wax is believed to migrate to the interlayer interfaces during processing of the film, and will crystallize  
5 in the amorphous regions of the polypropylene core layer and the adjacent layer interface areas.

The wax should have a molecular weight of from 300 to 1000 and preferably from 500 to 800. Melting points of such waxes are expected to be  
10 between 50°C to 140°C (122°F to 284°F), depending upon the chain length. An example of a polyethylene-type wax is POLYWAX brand wax available from Petrolite Corporation, which is a mixture of synthetic polyethylene of several molecular weights  
15 with a specified average molecular weight.

The amount of wax in the core layer can range from 0.25 percent to 15 percent of the total weight of the resin-wax blend. Higher amounts are impractical because of the difficulty in blending  
20 large quantities of wax with polypropylene, and are further discouraged to avoid problems with film shrinkage. It has been found that substantial improvements in MVTR with minimal shrinkage can be achieved with wax amounts below five percent,  
25 preferably between 0.25 and 3 percent, more preferably less than 2 percent, and most preferably between 0.5 and 2 percent.

#### Blending of Resin and Wax

Blending of the wax and core layer resin  
30 can be accomplished by conventional methods; the objective is to produce a homogenous blend. The two components can be separately fed in two streams into the feed throat of an extruder. Alternatively, they can be premixed in a blender (e.g., a Henschel  
35 mixer) and then weigh-fed into an extruder. Because



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of the bulk density differences and quite different melting behavior of the two ingredients, it is especially preferred to melt blend them to produce a concentrate of wax in a polyolefin carrier, which is then itself mixed with the core layer resin in the extruder hopper. A concentrate of about 15% wax in a carrier resin (e.g., PETROTHENE PP7300 polypropylene from Quantum Chemical Corporation, USI Division) has been found to work well. Preferred blending devices are twin screw extruders, kneaders, or similar intensive mixers, especially those equipped with underwater die face pelletizers.

#### Cap Layer

A polyolefin cap layer is provided on each side of the core layer. This cap can be the same as, but is preferably different than, the polypropylene of the core layer. The two cap layers can each be of the same or different material and thickness. The cap layers are preferably immediately adjacent to the core layer, but can also be separated by one or more intermediate layers of another resin or an adhesive. Additional layers may also be added to the exterior of the formed film.

The polyolefin is selected from propylene and ethylene polymers, copolymers, terpolymers or blends of these. Preferred polyolefins are selected from the group consisting of propylene homopolymer, ethylene homopolymer, copolymers of ethylene and propylene, copolymers of butene and propylene, copolymers of ethylene and alpha-olefins of ten or less carbon atoms, copolymers of ethylene and an unsaturated carboxylic acid, copolymers of ethylene and vinyl acetate, terpolymers of propylene, ethylene, and butene, and ionomers of ethylene and methacrylic acid.

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More preferred are polyolefins selected from the group consisting of ethylene and propylene, ethylene and vinyl acetate, and ethylene and unsaturated carboxylic acids. Especially preferred are random ethylene-propylene copolymers containing ten percent or less ethylene by weight, and a terpolymer of propylene, ethylene, and butene. Commercial sources of such polyolefins are well known in the art.

The cap layer does not contain added wax, although some may be present in that layer due to migration of the wax into and through the polymer. Any of the film layers in the structure may also include minor amounts of conventional additives such as antioxidants, pigments, slip agents, antiblocks, fillers, stabilizers, and the like. In some films, the slip agents or COF agents can comprise materials which increase film surface "slipperiness" and reduce the coefficient of friction of the film so that processing problems such as film breakage can be avoided. Examples of these are fatty acid amides, erucamides, oleamides, and silicones. Although according to this invention wax in the cap layers is unnecessary and is avoided, minor amounts (e.g., less than about 0.25 weight percent) of such additives in the cap layer are not expected to destroy the effect of improved MVTR and could be tolerated.

#### Film

Manufacturing multi-layered biaxially-oriented films can be accomplished by several different processes known to those in the art. One involves coextruding a cast composite sheet from a slot die. The sheet is then reheated and oriented in both the machine direction and the transverse

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direction, usually in two sequential steps, in the so-called stentor or "tenter" method. Simultaneous drawing in both directions is also possible.

5 In another method, layers can be added to a core layer by interdraw coatings or laminations. In yet another method, a thick multi-layered blown film tube from an annular die is reheated and further inflated in the transverse direction and stretched in the machine direction. This process is  
10 the so-called "double bubble" method for manufacturing BOPP.

Regardless of the method used, the cap layers are to be added to the core layer early enough in the process so that high temperatures,  
15 typically employed during orientation in one or both directions, do not result in significant loss of wax from the core layer. Orientation may be carried out prior to addition of the cap layers, if desired. Cap layers can but need not be as thick as the core  
20 layer, and cap layers of 2 microns or less are sufficient and preferred.

Biaxial orientation of at least the core layer, and preferably the entire film, is an important aspect of the invention because an  
25 orientation itself results in an improvement in MVTR, as compared to, for example, as cast film without orientation.

#### Heat Treatment

After formation and orientation of the  
30 BOPP film, it is then subjected to a final heat treatment, such as in an oven or "hot room." It is believed that the heat treatment causes the wax to migrate from the core layer to the interface between the core and its adjacent layers.

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The temperature of the treatment should be below the melting point of the polypropylene and below that temperature at which distortion occurs in the film, thus typically below 150°C (302°F).

5 Treatment is preferably below a temperature which may cause shrinkage of the film, or about 110°C (230°F). Heat treatment should be conducted above the melting point of the wax, about 50°C (122°F) for preferred waxes.

10 The heat treatment should be from at least five minutes to several hours or more in length, with time dependent upon the temperature. The rate of MVTR improvement is initially rapid, with further improvement possible by extended treatment over one  
15 or more days. Increases in temperature generally lessen the time needed. The time chosen is preferably one sufficient to allow migration of wax to the interface of the core and adjacent layer, but not so long as to permit substantial migration to  
20 the outer surface of the film where the wax may interfere with the surface properties such as printability.

Heat treatment also has a beneficial effect by reducing the oxygen transmission rate of  
25 the film. The finished film can be expected to have good dimensional stability (low shrinkage) and tensile strength.

The following examples illustrate the benefits of the invention.

30

#### EXAMPLES

##### Experimental Conditions

Films were made from polypropylene containing various amounts of wax. The

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polypropylene was an isotactic homopolymer with a Melt Flow Rate ("MFR", ASTM D1238 condition F) of 1.8 as the monolayer in Comparisons A and 1-7, and as the core layer of the three-layer structure of Examples B and 8-14. POLYWAX 500 having a density of 0.93, a melting point of 88°C, and a molecular weight of 500, was added as a percent by weight of the resin/wax blend.

The cap (exterior) layers were formed from a 5 MFR ethylene-propylene copolymer having 6.5% ethylene content, and contained no wax.

During manufacture, the layers were passed through a slot die at 220°C to form a thick sheet. The sheet was heated to 120°C by passing through heated rolls, and then drawn about 500 percent in the machine direction to form a mono-axially oriented film. This film was heated further at 160°C in the tenter oven and stretched about 900 percent in the transverse direction. The three-layer film was cooled, trimmed, and wound into a roll.

Moisture vapor transmission rate (MVTR) was measured on a MOCON model 600 instrument. The data are reported in units of g/100 sq in/24 hours at conditions of 100°F and 90% relative humidity (ASTM F1249). To compensate for variations in film gauge, recorded MVTR data was normalized to 1.0 mils thickness, assuming that MVTR is inversely proportional to thickness.

#### Comparisons A to H

The comparisons in Table I show the MVTR characteristics of wax-containing monolayer BOPP films having a measured gauge between 0.61 and 0.71 mils.

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The films containing various amounts of POLYWAX 500 showed no improvement in the MVTR, on average, compared to the control "A" containing zero percent wax. If Comparison H is omitted as perhaps anomalous, the remaining films showed an improvement averaging only six percent. The gloss of the control was 94, while the gloss of the others ranged from 85 to 93, as measured with Pacific Scientific's 45° Glossgard II Glossmeter using ASTM D2457. Haze of the control was 0.4, compared to a range of 0.7 to 2.3 for the others. Film haze measurements followed ASTM D1003 using a Gardner Hazeguard instrument.

TABLE I

## MONOLAYER FILM

| Film | % Wax | MVTR |
|------|-------|------|
| A    | None  | .25  |
| B    | 1.1   | .22  |
| C    | 2.1   | .26  |
| D    | 3.1   | .23  |
| E    | 4.2   | .23  |
| F    | 5.0   | .29  |
| G    | 6.3   | .24  |
| H    | 7.5   | .33  |

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Examples 1 to 8

These examples show the MVTR properties of a three-layer film with cap layers on each side of a polypropylene core layer which incorporates various amounts of POLYWAX 500. The film has the structure A/B\*/A (where "\*" denotes presence of wax). The cap layers "A" contained no wax. Films had a measured gauge between 0.68 and 0.82 mils.

As shown in Table II, the average MVTR of the films containing wax fell 77% compared to the control containing zero percent wax. This MVTR change from 0.24 to 0.059 (normalized to 1.0 mils) represents more than a four-fold improvement compared to three-layer films with no wax, and an even greater improvement over an uncapped monolayer BOPP film (see Table I), with or without wax.

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TABLE II

## THREE-LAYER FILM

| Film | % Wax | MVTR |
|------|-------|------|
| 1    | None  | .24  |
| 2    | 1.1   | .066 |
| 3    | 2.1   | .052 |
| 4    | 3.1   | .044 |
| 5    | 4.2   | .037 |
| 6    | 5.0   | .064 |
| 7    | 6.3   | .078 |
| 8    | 7.5   | .069 |

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Examples 9 to 12

Examples 9 through 12 illustrate the effect of wax in various layers of films, with results shown in Table III.

5           Example 9 had the structure B/B/A with no wax in any of the layers. The overall structure was 0.80 mils, with the core layer about 18 microns (about 0.72 mils) and the cap layers each representing about one micron (or about 0.04 mils).

10           Example 10 had a B\*/B/A structure where cap layer B\* contained 2.5 percent POLYWAX 500. Example 11 had a B\*/B\*/A structure with each of layers B\* having 2.5 weight percent POLYWAX 500. Example 12 was an A/C/B\*/C/A five-layer symmetric  
15 film of 0.78 total gauge, in which the two C-layers adjacent to the core are about one micron thick propylene homopolymers with no wax. The MVTR reduction effect still exists but is diminished.

TABLE III

## 20                           STRUCTURE VARIATIONS

| Film        | Structure  | % Wax | MVTR |
|-------------|------------|-------|------|
| 9           | B/B/A      | None  | 0.27 |
| 10          | B*/B/A     | 2.5   | 0.25 |
| 11          | B*/B*/A    | 2.5   | 0.27 |
| 25       12 | A/C/B*/C/A | 3.0   | 0.11 |

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Examples 13 to 16

Examples 13 through 16 (not tabulated) illustrate the wax concentrations effective at reducing MVTR. Three-layer BOPP films of total gauge ranging from 0.79 to 0.81 mils were made, with core layers having concentrations of POLYWAX 500 of zero, 0.5, 1.0, and 2.0 weight percent. The MVTR (normalized to 1.0 mils) was 0.30, 0.12, 0.07, and 0.06 respectively. Thus, an improvement in MVTR can be seen at 0.5% (or lower) wax concentration.

Examples 17-19

These examples demonstrate improvement in MVTR when a propylene copolymer is substituted for the propylene homopolymer of the core layer. Symmetrical three-layer films were made at 0.80 to 0.82 mils total thickness, of which the cap layers were 0.05 mils each. The core layer contained 3 MFR ethylene-propylene copolymer (PETROTHENE PP 7300 available from Quantum Chemical Corporation, USI Division), which contained 3% ethylene. Example 17 had no wax, whereas Examples 18 and 19 had 1.5% and 3% POLYWAX, respectively, in the core layer. MVTR data (not tabulated) normalized to 1.0 mils show that control (#17) at 0.45, while Examples 18 and 19 show 0.11 and 0.074, respectively.

Examples 20-27

These examples show the effect of using waxes with higher molecular weights under conventional BOPP tenter processing conditions.

Symmetrical three-layer BOPP films of structure A/B\*/A were made at 0.80 mils with the propylene homopolymer core of 0.70 mils containing 2.0 percent of selected linear polyethylene waxes. Petrolite POLYWAX products designated 500, 650, 800,

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1000, 2000, and 3000 were used, which have average carbon chain lengths of 36, 46, 61, 71, 143, and 214 with melting points of about 88, 100, 108, 114, 125, and 127°C, respectively. Only the film with POLYWAX  
5 500 showed any reduction in MVTR, at 0.20. The others had MVTRs equivalent to the control at about 0.37.

Examples 28-47

These examples show the additional  
10 improvement in MVTR after heat treatment. For the three layer films in Examples 28-47, columns in Table IV show the weight percent of wax in the core layer, the average molecular weight of the wax (POLYWAX), the temperature of the heat treatment,  
15 MVTR data (normalized to 1.0 mils) obtained before heat treatment, MVTR measured after two days at the stated temperature, and the percent improvement in the MVTR measurements.

Example 43 showed no improvement after two  
20 days, but improved 4% to an MVTR of 0.348 after eight days. No initial MVTR data are available for Ex. 45-46.

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TABLE IV

## HEAT TREATMENT

|    | Ex. | Wax<br>Per-<br>cent | Mol.<br>Wt.<br>Wax | Temp.<br>°F | MVTR<br>Initial | MVTR<br>@2<br>days | Per-<br>cent<br>Improv. |
|----|-----|---------------------|--------------------|-------------|-----------------|--------------------|-------------------------|
| 5  | 28  | -0-                 | -                  | 120         | 0.317           | 0.317              | 0                       |
|    | 29  | 1.0                 | 500                | "           | 0.317           | 0.122              | 61                      |
|    | 30  | 1.5                 | "                  | "           | 0.090           | 0.038              | 58                      |
|    | 31  | 1.75                | "                  | "           | 0.146           | 0.025              | 83                      |
|    | 32  | 2.0                 | "                  | "           | 0.100           | 0.033              | 67                      |
| 10 | 33  | 2.25                | "                  | "           | 0.084           | 0.027              | 67                      |
|    | 34  | 2.5                 | "                  | "           | 0.082           | 0.040              | 51                      |
|    | 35  | 3.0                 | "                  | "           | 0.114           | 0.025              | 78                      |
|    | 36  | 3.0                 | "                  | "           | 0.133           | 0.025              | 81                      |
|    | 37  | 1.5                 | 655                | 120         | 0.348           | 0.082              | 76                      |
| 15 | 38  | 2.5                 | "                  | "           | 0.348           | 0.054              | 84                      |
|    | 39  | 4.5                 | "                  | "           | 0.364           | 0.078              | 78                      |
|    | 40  | 2.0                 | 500                | 140         | 0.198           | 0.057              | 71                      |
|    | 41  | 2.0                 | 655                | "           | 0.364           | 0.079              | 78                      |
|    | 42  | 2.0                 | 800                | "           | 0.428           | 0.364              | 15                      |
| 20 | 43  | 2.0                 | 1000               | "           | 0.364           | 0.380              | -                       |
|    | 44  | -0-                 | -                  | 175         | 0.364           | 0.364              | -                       |
|    | 45  | 2.0                 | 500                | "           | -               | 0.277              | -                       |
|    | 46  | 2.0                 | 655                | "           | -               | 0.048              | -                       |
|    | 47  | 2.0                 | 800                | "           | 0.461           | 0.132              | 71                      |

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## CLAIMS

We claim:

1. A process for making a thermoplastic film, the process comprising:
  - 5 forming a blend of a resin and from 0.25 to 15 weight percent of a wax, the resin being selected from the group consisting of isotactic homopolymers of propylene, copolymers of propylene with up to fifteen percent ethylene or butene,  
10 terpolymers of propylene with ethylene and butene, and mixtures thereof, and the wax being crystalline and incompatible with the resin and having an average molecular weight from 300 to 1000;  
extruding the blend to form a core layer  
15 of a film;  
orienting the core layer in biaxial directions; and  
providing on each side of the core layer a polyolefin cap layer.
- 20 2. The process of claim 1 in which the wax is selected from the group consisting of paraffins and polyethylene waxes.
3. The process of claim 2 in which the blend is formed with from 0.25 to 3 percent wax.
- 25 4. The process of claim 3 in which the blend is formed with from 0.5 to 2 percent wax.

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5. The process of claim 4 in which the wax has an average molecular weight from 500 to 800.

6. The process of claim 1 which further comprises the subsequent step of heating the film at  
5 from 50°C to 150°C for at least five minutes.

7. The process of claim 6 in which the wax has an average molecular weight between 800 and 1000.

8. The process of claim 6 in which the  
10 film is heated at from 50° to 110°C.

9. The process of claim 6 in which the film is heated for at least one hour.

10. The process of claim 9 in which the film is heated for at least 24 hours.

11. The process of claim 1 in which the  
15 core layer is oriented after the cap layers are provided.

12. The process of claim 1 in which the  
20 cap layer is provided by coextrusion with the core layer.

13. The process of claim 1 in which the cap layer is provided by means of interdraw coating on the core layer.

14. The process of claim 1 in which the  
25 thickness of each cap layer is less than 2 microns.

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15. The process of claim 1 in which the resin is selected from the group consisting of isotactic homopolymers of propylene and copolymers of propylene with up to six percent ethylene or  
5 butene.

16. The process of claim 15 in which the resin is an isotactic homopolymer of propylene.

17. The process of claim 15 in which the cap layer is selected from the group consisting of  
10 random ethylene-propylene copolymers with up to ten percent ethylene, copolymers of propylene with butene, and terpolymers of propylene, ethylene, and butene.

18. The film made by the method of claim  
15 1.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/09671

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : Please See Extra Sheet.

US CL : 264/171

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/171, 235.8, 290.2; 156/244.11

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y         | US, A, 5,141,801(TAKESHITA ET AL) 25 AUGUST 1992, abstract, claims 1-10            | 1-18                  |
| Y         | US, A, 5,155,160 (YEH ET AL) 13 OCTOBER 1992, abstract, claims 1-14                | 1-18                  |
| Y         | US, A, 4,870,122 (LU) 26 SEPTEMBER 1989, abstract                                  | 1-18                  |
| Y         | JP, A, 49-47,478 (TOYOBO) 08 MAY 1974 , abstract                                   | 1-18                  |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

|   |  |
|---|--|
| * Special categories of cited documents:  | *T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention   |
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| *O* document referring to an oral disclosure, use, exhibition or other means  |  |
| *P* document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

14 NOVEMBER 1994

Date of mailing of the international search report

DEC 02 1994

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/09671

A. CLASSIFICATION OF SUBJECT MATTER:  
IPC (5):

B29C 47/06